

Impact of Sulfonated Acetone Formaldehyde (SAF) on the Durability of SRC–SF Composite Cement Pastes

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ABSTRACT

This work aimed to study the effect of the dosage of laboratory synthesized Sulfonated Acetone Formaldehyde (SAF) on the hydration characteristics of sulfate resisting cement (SRC) pastes incorporating 10 mass% SF and hydrated up to 90 days. Initial and final setting times, compressive strength, bulk density, total porosity and hydration kinetics were determined. The values of combined water, compressive strength and bulk density increase with polymer content up to 1.5 mass% (optimum mix) this is intrinsically associated with slightly reduction of W/C ratio with polymer content as well as the improvement of superplasticizing effect of SAF addition. IR spectra are in a good agreement with the results of physico-chemical and mechanical properties. The synthesized SAF condensate could improve the bulk density and compressive strength of the investigated cement pastes.

Key Words: Accelerator; Hydration characteristics; Superplasticizers; Compressive strength; Bulk density; SAF.

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1. INTRODUCTION

Water-soluble polymer used in the construction industry is known as a superplasticizer. The superplasticizers are organic polyelectrolytes that are polymeric dispersants. They are classified according to their chemical compositions as sulfonated synthetic polymers, carboxylated synthetic polymers, and synthetic polymers with mixed functionality. Water-soluble polymers such as sulfonated phenolic resin (SPF), water-soluble acrylate/sulfonated copolymer and sulfonated acetone formaldehyde (SAF) have also been used successfully in concrete. One of the main areas of application of water-soluble polymers is its use in the production of self-compacting concrete.

The water–cement system is highly sensitive to superplasticizers addition of small amounts of superplasticizers enhance the efficiency of workability properties, but they often associated with strong, undesired retardation phenomena of the setting of the cement paste [1-8].

Only a small amount of superplasticizer can significantly improve the workability, mechanical strength, and other properties of concrete [5-8]. The roles of this water-soluble polymer are to (1) improve the rheological properties of fresh concrete without segregation or bleeding; (2) act as a lubricant or a dispersing agent so that solid particles become more uniformly dispersed; (3) interact with cement or hydrated products to modify the morphology of materials; and (4) make hardened concrete stronger or more durable [8–14].

One key to the preparation of durable concrete is the addition of high range of water reducing superplasticizer. They are widely used in concrete industry and are known as the fifth component of concrete, besides cement, sand, gravel and water, because these admixtures have been found beneficial in offsetting some of undesirable characteristics of concrete especially in hot climate [9–15].

Sulfonated naphthalene formaldehyde condensates (SNF) and sulfonated melamine formaldehyde condensates are two typical examples. These admixtures, after being adsorbed on cement particles, create electrostatic repulsions and overcome attractive forces, and cause the dissociation of the cement agglomerates into primary particles. As a result, they provide good dispersing effect on cement and are able to reduce water demand of concrete up to 30%, while maintaining the flow characteristics [16–18]. Currently, a new generation of SPs based on polycarboxylate polymers with long, comb-type side chains (PC) has been developed. These chemicals are more effective for the water reducing capability and for preventing slump loss, for they can disperse cement particles not only by electrostatic repulsions aforementioned, but also by steric hindrance effects [19].

Although PC could maintain the workability of concrete for a long period of time, its applications in preparing flowing concrete and high performance concrete are limited due to economic reasons. In other words, SNF is still the main SP used instead because of the relatively low cost. However, care must be taken to prevent rapid slump loss of concrete when SNF was incorporated.

Recently, Lim et al. [20] mentioned that polycarboxylic acid polymer with -COO^- functional group could cause a slump-releasing effect. They reported that addition of 20 wt. % of a copolymer of maleic anhydride and acrylic acid in SNF showed an excellent control of effect of slump loss of cement pastes and increasing apparent viscosity.

Because superplasticizers are one of the most important ingredients used in concrete, the research and development of superplasticizer have attracted great attention recently [21-29].

The aim of the present investigation is to evaluate the effectiveness of laboratory synthesized SAF condensate on the durability of SRC pastes incorporating 10% SF.

2. MATERIALS AND METHODS

2.1. STARTING MATERIALS:

The materials used in this investigation were sulphate resisting cement (SRC) provided from El-masria Cement Company, and condensed silica fume (SF) from Ferrosilicon Alloys Company, (Edfo, and Aswan, Egypt). The chemical composition of starting materials is shown in Table (1).

Table 1. Chemical analysis of starting materials, (wt%).

Oxides Material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	I.L	Total
SRC	21.40	3.67	5.05	64.73	1.50	2.05	0.30	0.22	2.60	99.70
Silica fume	94.81	0.16	0.84	0.89	0.49	0.08	0.20	0.05	2.43	99.95

2.2. THE MINERALOGICAL COMPOSITION:

The XRD pattern of silica fume is shown in Figure (1). It indicates that the silica fume is completely amorphous; exhibiting only a very broad scattering peak. Figure (2) shows the IR spectra of SF. The spectrum of SF shows the strongest absorbance bands at 1123, 806, and 483 cm⁻¹, characteristic of condensed silica. The broad band centered at 1123 cm⁻¹ is attributed to asymmetric stretching frequency of Si-O-Si, the band centered at 806 cm⁻¹ is due to symmetric stretching of Si-O-Si, and the band at 483 is due to the bending frequency of O-Si-O [30].

The surface area of SRC determined by the Blaine air permeability method, was found to be 3488 cm²/g whereas that of silica fume is about 20 m²/g

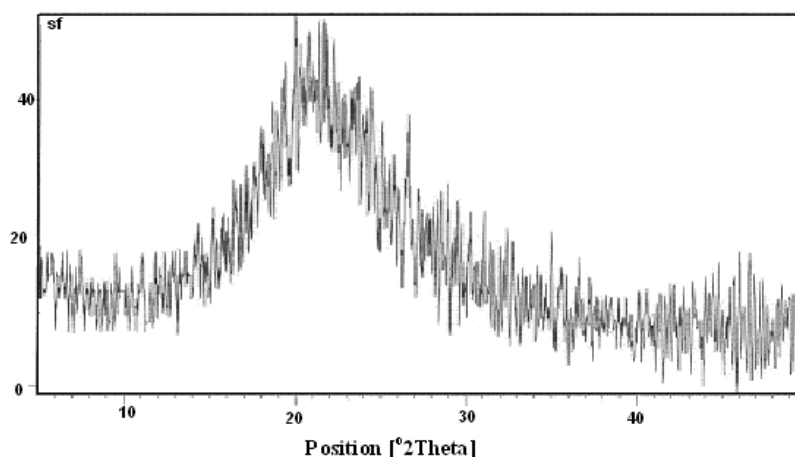


Figure 1. XRD pattern of silica fume

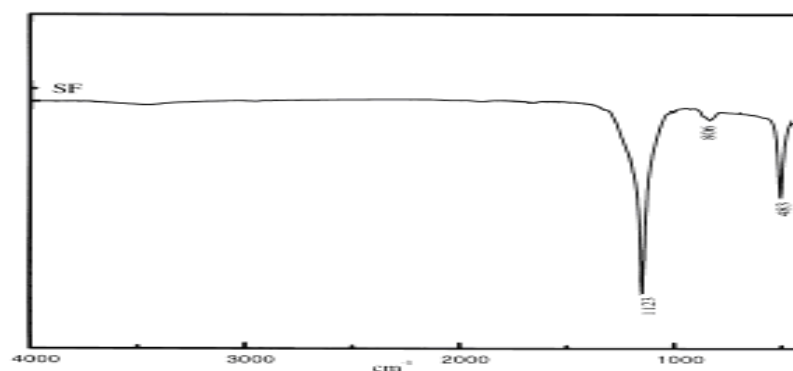


Figure 2. IR spectra of Silica fume

2.3. PREPARATION OF SULFONATED ACETONE–FORMALDEHYDE (SAF) RESIN:

Sodium bisulfite was dissolved in water in a jacketed reactor flask equipped with a baffle stirrer and a reflux condenser at 50 °C. The temperature of the solution was maintained at 50 °C till the solution is appeared clear. As soon as the solution became clear, the temperature was decreased to 40 °C and acetone was added. The reaction was then carried out at 40 °C for 1 h. Formaldehyde aqueous solution of 37 wt% concentrations was fed into the reactor through a dropping funnel. During the feeding process, the temperature of the reaction was automatically increased up to 60–65 °C. The reaction continued at 60–65 °C for another one hr when the feeding of formaldehyde is finished. The temperature was raised to 85 °C and the reaction continued for 4 h. After cooling, the resin prepared according to the above procedure has a solid content of approximately 40 wt% and the final pH of the red-brown solution is above 12. The synthetic process is shown in Figure (3) and the chemical structure of SAF resin is shown in Figure (4) [14].

The structure of the accelerator was confirmed via fourier Transform Infrared, ATI Mattson Genesis, FTIRTM spectrophotometric analysis.

The mix composition of the prepared silica-fume blended cement with admixtures is shown in Table (2).

Table 2. Mix composition of the investigated mixes, (wt %).

Sample No.	Doses of (SAF)	SRC	SF
S ₀	0.0	90	10
S ₁	0.50	90	10
S ₂	1.00	90	10
S ₃	1.50	90	10
S ₄	2.00	90	10

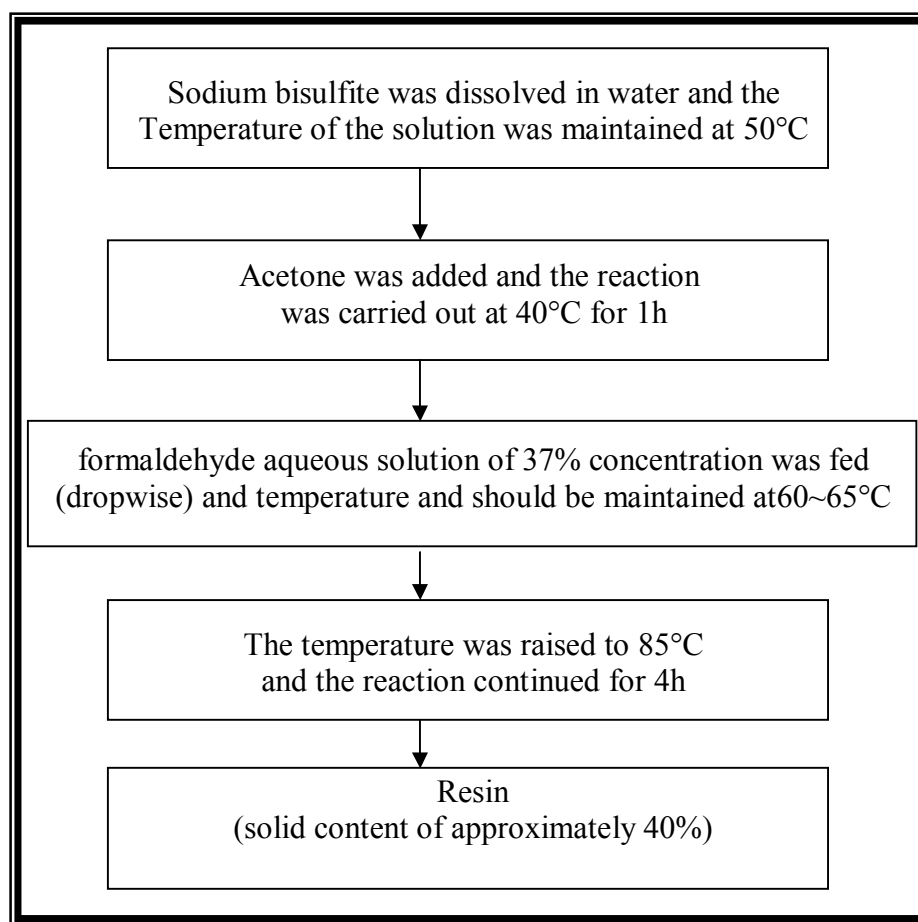


Figure (3): Synthetic process of SAF resin

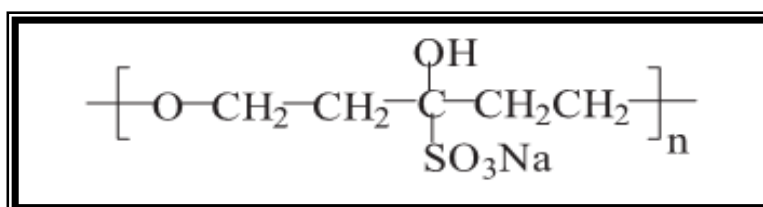


Figure (4): The molecular structure of SAF resin

2.4. PREPARATION OF CEMENT PASTES:

2.4.1. PREPARATION OF DRY MIXES:

The ingredients of each mix of Sulphate resisting cement (SRC) and 10 wt% silica fume were mixed for one hour with four balls using a mechanical roller to assure complete homogeneity. The samples were kept in airtight container.

2.4.2. MIXING OF CEMENT PASTE:

The required amount of each dry mix was placed on a smooth, non-absorbent surface and a crater was formed in the center. The required amounts of mixing water as water of consistency containing the admixture with different dosages (0.0, 0.5, 1.0, 1.5 and 2.0% of the

water-admixture) were poured into the crater and the cement on the outer edges was turned into the crater by the aid of a trowel. The dry cement around the outside of the crater was slightly troweled over the mixture to absorb the water for about one minute. The mixing operation was then completed by continuous vigorous mixing for about three minutes by means of gauging trowel.

2.4.3. MOULDING:

Stainless steel ½ inch cubic moulds were used to prepare the cement pastes. Freshly prepared cement paste was placed in the moulds into two approximately equal layers. Each layer was compacted and manually pressed until homogeneous specimen was obtained. After the top of the layer was compacted, the moulds were then vibrated for a few minutes to remove any air bubbles to get a better compaction of the prepared pastes. The surface of the paste was smoothed by the aid of thin edged trowel.

2.4.4. CURING:

Immediately after moulding, the moulds were cured in humidity chamber at about 100% relative humidity at room temperature $23 \pm 1^\circ\text{C}$ for 24 hrs then demoulded and cured under tap water up to study the hydration characteristics after one, 3, 7, 28, 90 days.

2.5. METHODS OF INVESTIGATION:

2.5.1. WATER OF CONSISTENCY AND SETTING TIME:

The water of normal consistency and the initial as well as final setting times were determined according to ASTM methods [31] using Vicat Apparatus. The quantity of water required to produce a paste of standard consistency will be that required to give a paste which permitted the settlement of the Vicat plunger (10 mm. in diameter) to a point 5 to 7 mm from the bottom of the Vicat mould. The plunger was replaced by the needle of initial setting time then lowered gently into contact with the surface of the paste. This process would be repeated until the needle did not penetrate beyond about 5-7 mm from the bottom of the mould. The period between the addition of water to the cement and the time at which the needle ceased to penetrate the paste beyond 5-7 mm, defined as the "initial setting time".

The final setting time was determined with the aid of needle with an annular attachment. When the paste was soft, both the needle and the attachment made an impression on the surface when released. The final set was said to attain when only the needle made such an impression. The period between the first contact with water to the cement and the time of the final set is defined as the "final setting time".

2.5.2. BULK DENSITY MEASUREMENT:

The bulk density was carried out before the specimens subjected to compressive strength determination. Bulk density was determined through weighing the samples of hardened pastes (suspended in water) and in air (saturated surface dry). Each measurement was conducted on at least three similar cubes of the same age. The following equation was used for calculating the bulk density [32]:

$$\text{Bulk density (BD)} = \frac{\text{Saturated weight}}{\text{Volume of sample}} \quad \text{g/cm}^3$$

$$\text{Volume of sample} = \frac{\text{Saturated weight} - \text{suspended weight}}{\text{Density of liquid (water)}} \quad \text{cm}^3$$
$$\text{Bulk density (BD)} = \frac{\text{Saturated weight}}{\text{Saturated weight} - \text{suspended weight}} \quad \text{g/cm}^3$$

2.5.3. TOTAL POROSITY MEASUREMENT:

After the determination of bulk density (BD), the three similar cubes of the same age were dried in a furnace at 105°C for 24 hours then weighed in air after cooling in a desiccator. The total porosity of the hardened cement pastes could be calculated as follows:

$$\text{Total porosity, \%} = \frac{\text{Saturated weight} - \text{dried weight}}{\text{Saturated weight} - \text{suspended weight}} \times 100$$

2.5.4. STOPPING OF THE HYDRATION:

The non-evaporable water is used as an indication for the degree of hydration of the hydrated samples after a given period. Since the non-evaporable water is retained in the sample after the free water is removed, so the free water must be removed. The removal of free water was accomplished by drying the saturated cement pastes at 105°C for 24 hrs.

2.5.5. COMPRESSIVE STRENGTH MEASUREMENT:

A set of three cubes was used for the determination of compressive strength of hardened cement paste [33]. The compressive strength measurements were done on a compressive strength machine of SEIDNER, Riedinger, Germany, with maximum capacity of 600 KN force.

2.5.6. DETERMINATION OF FREE LIME:

The free lime content of any hydrated or heat treated cement paste can be determined by thermal process. Approximately 0.5 g of the cement paste was placed in a porcelain crucible and introduced into a cold muffle furnace. The temperature was gradually increased up to 390 then to 550°C at heating rate of 3°C/min. The loss of weight occurred between 390 - 550°C and soaking time of 15 min is the weight of water from the decomposition of calcium hydroxide. Therefore, the free lime can be calculated.

2.5.7. DETERMINATION OF COMBINED WATER:

Parts of the broken samples from the compressive strength measurement were taken and saturated through moistened paper tissue. Two representative samples of the dried specimen about 2g each were exactly weighed in a porcelain crucibles and ignited in a muffle for one hour at 950°C [34], cooled in a desiccator, then weighed. The combined water content was calculated using the following equation:

$$\text{Combined water, \%} = \frac{\text{Weight before ignition - weight after ignition}}{\text{Ignited weight}} - L$$

Where: L is the ignition loss of unhydrated specimen.

2.5.8. X-RAY DIFFRACTION TECHNIQUE (XRD):

The XRD technique was carried out using BRUXER, Axs D8 ADVANCE A8, GERMANY Diffractometer. The sample was finely ground to pass a 200-mesh sieve. The identification of samples was confirmed by computer-aided search of the PDF database obtained from the Joint Committee on Powder Diffraction Standards-International Center for Diffraction Data (JCPDS-ICDD), 2001. [35]

2.5.9. INFRARED SPECTROSCOPIC ANALYSIS (IR):

The infrared spectrum of compound can be used as a finger print to provide qualitative and quantitative analysis of mixture [36]. Infrared spectral analysis was carried out on some selected 3 samples of hydrated pastes to provide additional information on the hydrated products. It is sometimes possible to have conclusions concerning aspects of the structures from their appropriate spectrum.

The samples were prepared using alkali halide pressed disk technique as it gives a further reduction in scattering [37]. 2 mg of the powder sample was ground with 198 mg of potassium bromide in an agate mortar to produce a homogeneous mixture (as in the preparation of a mull, scattering is reduced if the sample is very finely ground). The mixture pressed under vacuum to give a transparent disc of 1 cm in diameter. Care is required to avoid breaking the KBr disc. Transfer the KBr disc to a sample holder and place in the spectrometer. The infrared spectral analysis was recorded from KBr-discs using Genesis -IR spectrometer in the range 400-4000 cm^{-1} .

3. RESULTS AND DISCUSSION

3. 1. HYDRATION CHARACTERISTICS:

3.1. 1. WATER OF CONSISTENCY AND SETTING TIME:

The water of consistency is the gauging water required to bring the cement pastes to standard consistency. The setting is the term used to describe the stiffening of the cement paste. The setting time is defined as the time which elapses between mixing the cement with water and the time when the paste will resist a creation arbitrary fixed pressure. It serves, however, for the comparison of the setting properties of the different cements. Two periods are distinguished, "initial set" or interval between the gauging and partial loss of plasticity, and the "final set" is the time required for the gauged cement to acquire sufficient firmness to resist a certain definite pressure.

The determination of setting time is affected to a marked degree by the quantity of mixing water, temperature, and other factors such as the surface area, the chemical admixture and chemical composition of the cement [38].

The cement pastes were prepared by addition of sulfonated acetone-formaldehyde (SAF) to the mixing water by ratios of 0.0, 0.5, 1.0, 1.5 and 2.0 wt % of cement, respectively.

The water of consistency, initial and final setting times of the different cement pastes with various ratios of sulfonated acetone–formaldehyde (SAF) accelerator are shown graphically in Figure (5a). It is clear that the water of consistency tends to decrease with the increase of the dosage of SAF. Also, the initial and final setting times are accelerated by the addition of SAF. As the dosages of SAF increases the initial and final setting times decrease. This is due to the accelerating effect of SAF.

Superplasticizers are effective in breaking and dispersing the cement particle networks, preventing premature linkage as well as minimizing the amount of standard water of consistency required to suspend the particles and render the mix workable. The admixtures control the forces between particles and increase fluidity of the mix. As a result of this, less water is required to achieve a given consistency. These polymeric materials are adsorbed on cement particles, forming a good ionic repulsion raised from the negative charge of sulphonate groups, consequently increasing its fluidity [25-29].

3.1. 2. BULK DENSITY:

The results of bulk density of the cement pastes admixed with various dosages of SAF cured up to 90 days are graphically illustrated as a function of curing time in Figure (5b).

It is clear that as the curing time proceeds, the bulk density increases for all hardened cement pastes. As the hydration proceeds more hydration products are formed which fill up some available open pores [39-44], therefore, the bulk density increases [40, 45, 46].

As the amount of the SAF increases up to 1.5 wt% the bulk density increases due to the filling effect and the acceleration of hydration, i.e. more hydration products are formed and then the pores decrease between the cement particles to produce more compact structure. The decrease of the available pores increases the efficiency of pozzolanic reaction of silica fume, due to approaching the silica fume grains from liberated $\text{Ca}(\text{OH})_2$ to produce additional amounts of calcium silicate hydrates, hence the bulk density increases. Increase the amount of SAF up to 2.0wt% the bulk density decreases, this is due to the retardation effect.

3.1.3. TOTAL POROSITY:

The total porosity values of the cement pastes admixed with different dosages of SAF, such as 0.0, 0.5, 1.0, 1.5 and 2.0 wt% as a function of curing time up to 90 days are illustrated in Figure (5c). It is clear that for all dosages the total porosity decreases with curing time up to 90 days. This is mainly due to the continuous hydration of cement pastes forming hydration products precipitated in the open pores of the cement pastes. This leads to the decrease of total porosity [47, 48].

On the other side, as the amount of SAF increases up to 1.5wt% the corresponding total porosity decreases. This is due to the acceleration of hydration which forming more hydration products precipitated in the open pores of the cement pastes.

The addition of 2.0wt% SAF increases the total porosity due to the retardation effect. The accelerator may coat the cement particles which retards the hydration of cement paste. This leads to decrease the hydration products precipitated in some of the open pores, therefore, the total porosity increases.

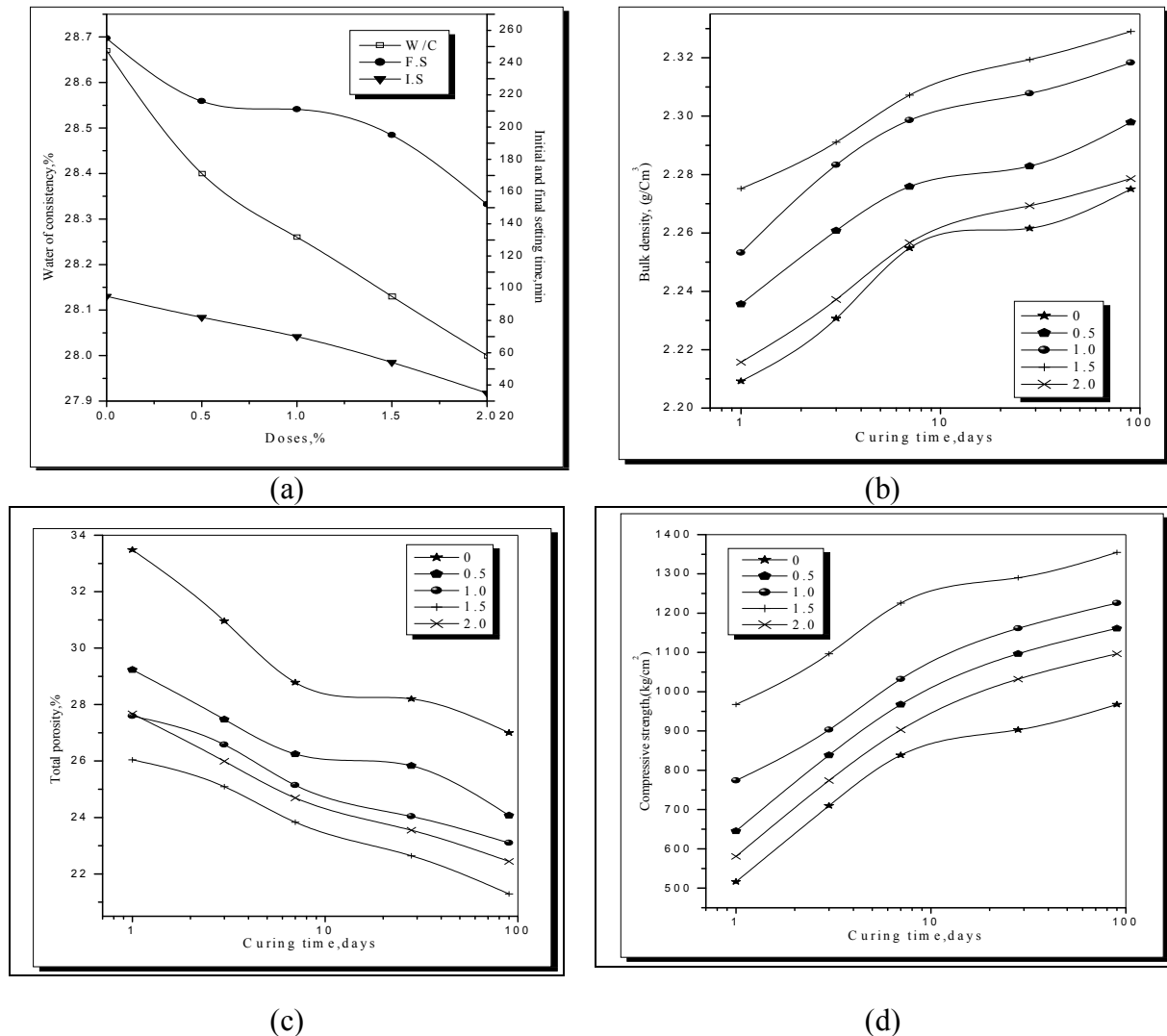


Figure 5. 5a: Water of consistency, initial and final setting time; 5b: Bulk density; 5c: Total porosity; 5d: Compressive strength of cement pastes in presence of different dosages of SAF as a function of curing time

3. 1.4. COMPRESSIVE STRENGTH:

The compressive strength values of the hardened cement pastes admixed with different dosages of SAF, such as 0.0, 0.5, 1.0, 1.5 and 2.0 wt % as a function of curing time up to 90 days are graphically represented in Figure (5d). It is clear that for all dosages the compressive strength increases with curing time. This is mainly due to the increase of the amount of hydration products especially tobermorite-like gel (C-S-H) which is the main source of the strength [49, 50].

As the hydration proceeds, more hydration products are formed and filling the open pores leading to an increase of the compressive strength of the cement pastes. The hydration products possess a large specific volume than unhydrated cement components, therefore the accumulation of the hydrated products fill a part of originally filled spaces (pores). This leads to a decrease of the total porosity of the cement paste. The increase in the extent of hydration as measured by the chemically-combined water content and the decrease of the total porosity with hydration time, work together leading to increase the ultimate compressive strength. As the amount of SAF increases up to 1.5 wt% the compressive strength increases. This is mainly

due to the acceleration of hydration which increases the amount of hydration products especially tobermorite-like gel (CSH) [51, 52]. The addition of 2.0wt% SAF decreases the compressive strength due to the retardation effect as well as the increase of total porosity and decrease of bulk density. In spite of the decrease of the water of consistency at 2.0%, the compressive strength decreases, this may be due to the coating of the accelerator on the cement grain at 2.0 wt% which delays the hydration and then the strength decreases.

3. 1.5. THE CHEMICALLY COMBINED WATER CONTENT:

The combined water content changes as a result of the amount and type of hydration products. Although the combined water can be decreased with curing time of cement pastes due to the transformation of the hydration products of high lime to the lower lime content [53]. The combined water content generally increases with curing time due to the progress of the hydration and formation of hydration products which have high combined water contents such as CSH, C_4AH_{13} , C_2ASH [54].

The Chemically combined water contents of the cement pastes admixed with various dosages of SAF cured up to 90 days are graphically plotted in Figure (6a). The results show that the chemically-combined water content increases gradually with curing time up to 28 days for all cement pastes. This is due to the progress of the hydration and the pozzolanic reaction of silica fume with the liberated lime forming more hydration products. The combined water contents decrease at 90 days due to a release of water during polymerization of silicates [55, 56]. Moreover, this may be related to the transformation of the initially formed high-lime CSH with higher combined water content, to low-lime CSH, which has low combined water content.

As the amount of SAF increases up to 1.5wt% the chemically combined water contents increase due to the acceleration of hydration. This leads to increase the amount of hydration products. The combined water contents decrease at 2.0wt% SAF due to the retardation effect.

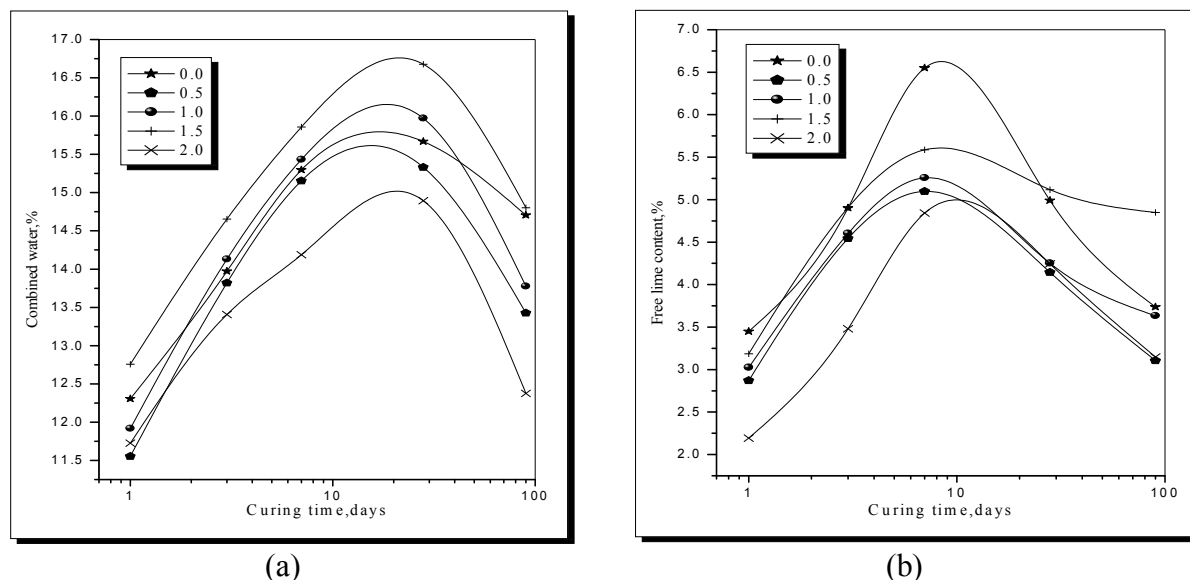


Figure 6. 6a: Chemically combined water content; 6b: Free lime of cement pastes in presence of different dosages of SAF as a function of curing time

3. 1.6. FREE LIME CONTENT:

The free lime contents of the cement pastes admixed with various dosages of SAF cured up to 90 days are plotted in Figure (6b).

The free lime contents of the cement pastes admixed with various dosages of SAF increase up to 7 days, then decrease up to 90 days for all dosages of SAF. The free lime increases at the early age up to 7 days due to that the rate of liberation is higher than the rate of consumption with silica fume therefore the free lime content increases. After 7 days up to 90 days the free lime decreases sharply due to the higher pozzolanic activity of silica fume or the rate of consumption is higher than that of liberation. As the amount of SAF increases up to 1.5wt% the free lime contents increase due to the acceleration of hydration. This leads to increase the amount of hydration products and free lime. The addition of 2.0wt% SAF the free lime contents decrease due to the retardation effect as previously discussed that decreases the hydration products and free lime.

3. 1.7. IR SPECTROSCOPY:

The IR spectra of cement pastes admixed with various dosages of sulfonated acetone formaldehyde (SAF) such as 0.0, 1.0 and 2.0wt% determined at 7 days are shown in Figure (7a). The band at 979cm^{-1} is due to silicate group [57]. A characteristic absorption band at 1127cm^{-1} was observed and composed mainly of SiO_2 . The band at 3439cm^{-1} is attributed to stretching of hydroxyl groups associated with water in calcium silicate hydrate [58]. In addition, the band at 1650cm^{-1} is related to the bending of H_2O and indicates the formation of CSH [59]. The band at 1506cm^{-1} is due to carbonate. The very sharp band illustrated at 3735cm^{-1} [60,61] represented the free lime. From the figure it is clear that the bands at 3735 and 3439 as well as 1650cm^{-1} represent the free lime and hydration products show higher intensity at 1.0wt% SAF. This is due to the acceleration of hydration which forming more hydration products and free lime. But these bands are lower at 2.0wt% SAF due to the retardation effect. On the other hand, the band appears at 979cm^{-1} due to the symmetric stretching of bands O-Si-O and O-Al-O [62] shows higher intensity at 1.0wt% SAF due to acceleration effect but it is lower at 2.0wt% SAF due to the retardation effect.

Figure (7b) shows the IR spectra of cement pastes admixed with various dosages of SAF such as 1.0 and 2.0wt% determined at 90 days. The bands at 3735, 3439 and 1650 as well as 979cm^{-1} represented the free lime and hydration products show higher intensity at 1.0wt% SAF due to acceleration effect but these bands are low at 2.0wt% SAF due to the retardation effect.

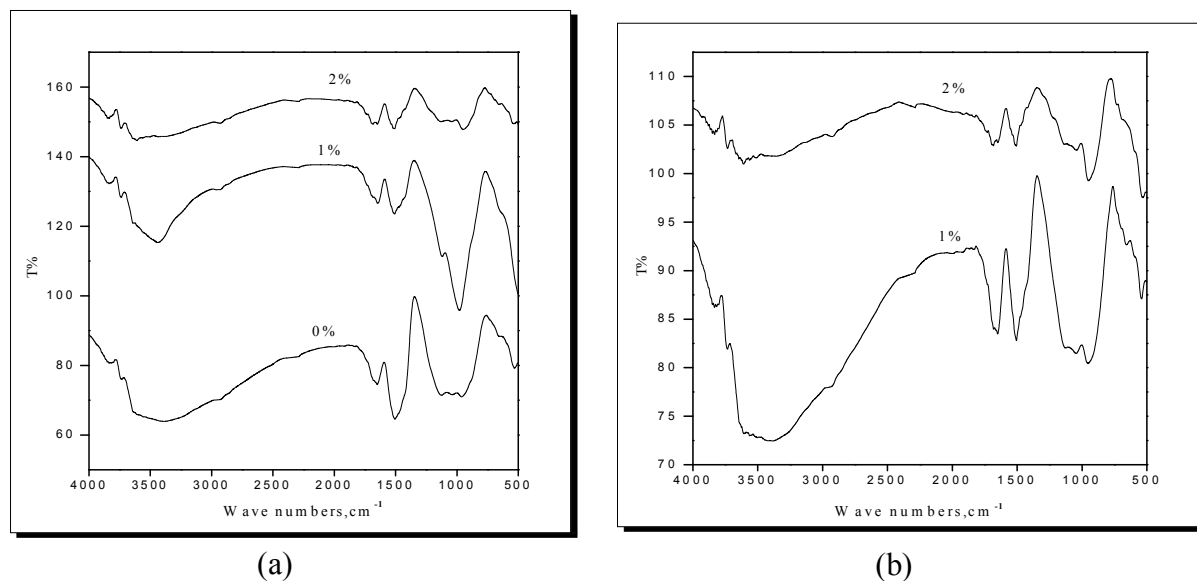


Figure 7. IR of cement pastes in presence of different dosages of SAF determined. 7a: at 7 days; 7b: at 90 days

CONCLUSION

Based on the results of experimental study concerning the effectiveness of laboratory prepared SAF superplasticizer dosage up to 2 mass% on the hydration kinetics, total porosity, bulk density, compressive strength and durability of SRC pastes containing 10% SF cured in tap water. Several recommendations and conclusions can be derived and presented as follows:

1. It is clear that the water of consistency tends to decrease with the increase of the dosage of SAF. Also, the initial and final setting times are accelerated by the addition of SAF.
2. With curing time, the compressive strength and bulk density increase, whereas the total porosity decrease for cement pastes admixed with different superplasticizer dosages.
3. The cement paste admixed with 1.5 mass % SAF has the highest bulk density and compressive strength up to 90 days in tap water.
4. As the amount of SAF increases up to 1.5wt% the free lime contents increase due to the acceleration of hydration. This leads to increase the amount of hydration products and free lime. The addition of 2.0wt% SAF the free lime contents decrease due to the retardation effect as previously discussed that decreases the hydration products and free lime.

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